

**IN THE SPECIFICATION**

Please amend the following paragraphs in the specification. For the Examiner's convenience, this Amendment includes replacement paragraphs with markings to show changes relative to the immediate prior version of each currently amended paragraph.

**INSERT the following paragraph after the Title on Page 1:**

This is continuation of co-pending U.S. Patent Application Serial No. 09/921,183, filed August 3, 2001, which is a divisional of U.S. Patent Serial No. 09/841,253, filed April 25, 2001, (abandoned), which is a divisional of U.S. Patent Application Serial No. 09/209,932, filed July 8, 1998, (now U.S. Patent No. 6,254,978), which is a continuation of U.S. Patent Application Serial No. 08/903,844, filed July 31, 1997, (abandoned), which is a file-wrapper-continuation of U.S. Patent Application Serial No. 08/339,425, filed November 14, 1994, (abandoned).

**REPLACE the paragraph beginning on Page 1, Line 25 with the following:**

These membranes must have sufficient strength to be useful in their various applications. Often this need for increased strength requires the membranes to be made thicker which decreases their ionic ~~conductivity~~ conductance. For example, ion exchange membranes that are not reinforced such as those commercially available from E.I. DuPont de Nemours, Inc. and sold under the trademark Nafion are inherently weak at small thicknesses (e.g., less than 0.050 mm) and must be reinforced with additional materials causing the final product to have increased thickness. Moreover, these materials cannot be reliably manufactured pinhole free

**REPLACE the paragraph beginning on Page 2, Line 27 with the following:**

U.S. Patent 5,082,472 to Mallouk, et al. relates to a composite membrane of microporous film in laminar contact with a continuous perfluoro ion exchange resin layer wherein both layers

have similar area dimensions. Surfaces of internal pores of ePTFE may be coated at least in part with perfluoro ion exchange resin coating, or the pores in the microstructure may be filled or partially filled with resin. The membrane of ePTFE had a thickness of about 2 mils (0.050 mm) or less and the perfluoro ion exchange layer in its original state had a thickness of about 1 mil (0.025 mm). The ePTFE layer of this composite membrane imparted mechanical strength to the composite structure and the pores of the ePTFE were preferably essentially unfilled so as to not block the flow of fluids.

**REPLACE the paragraph beginning on Page 3, Line 20 with the following:**

U.S. Patent 4,865,925 to Ludwig, et al. relates to a gas permeable electrode for electrochemical systems. The electrode includes a membrane located between and in contact with an anode and a cathode. The membrane, which may be made of expanded polytetrafluoroethylene, may be treated with an ion exchange ~~membrane~~ material with the resulting membrane maintaining its permeability to gas. Membrane thicknesses are described to be between 1 and 10 mils, (0.025-0.25 mm), with thicknesses of less than 5 mils (0.125) to be desirable. Examples show that membrane thicknesses range from 15 to 21 mils.

**REPLACE the paragraph beginning on Page 4, Line 20 with the following:**

An ultra-thin integral composite membrane is provided including a porous polymeric membrane having a structure of micropores of polymer with a porosity of greater than 35%, an average pore diameter of less than 10 microns and a thickness of at most 0.025 mm and a perfluoro ion exchange polymer impregnated within the micropores so as to render the micropores substantially occlusive, wherein the composite membrane is impermeable to gases and liquids and is substantially free of pinholes. Porous polymeric membranes suitable for this invention include membranes made of perfluoroalkyloxy resin, fluorinate ethylene propylene,

polyolefins, polyamides, cellulotics, polycarbonates, and fluorinated and chlorinated polymers ~~and polysulfones~~. Perfluoro ion exchange materials suitable for use with this invention include perfluorinated sulfonic acid resin, perfluorinated carboxylic acid resin, polyvinyl alcohol, divinyl benzene, and styrene based polymers. A reinforcement backing may also be provided.

**REPLACE the paragraph beginning on Page 5, Line 17 with the following:**

An ultra-thin composite membrane is provided and includes a base material of microporous membrane with a thickness less than 1 mil (0.025 mm) having a microstructure of micropores and perfluoro ion exchange resin that substantially impregnates the microporous membrane so as to occlude the micropores. The ultra-thin composite membrane may be employed in many different types of applications including for example, chemical separation, electrolysis in fuel cells and batteries, pervaporation, gas separation, dialysis separation, industrial electrochemistry such as chlor-alkali, and other electrochemical devices, catalysis as a super acid catalyst and use as a ~~catalyst support in~~ medium of enzyme immobilization.

**REPLACE the paragraph beginning on Page 5, Line 36 with the following:**

The microporous membrane which serves as the base material for the composite has a porosity of greater than 35% and preferably has a porosity of between 70-95%. The pores of the microstructure have a diameter less than 10  $\mu\text{m}$ , are preferably between 0.05 and 5  $\mu\text{m}$ , and are most preferably about 0.2  $\mu\text{m}$ . The thickness of the membrane is at most 1 mil (0.025 mm) preferably between 0.06 mils (0.19  $\mu\text{m}$ ) and 0.8 mils (0.02 mm), and most preferably between 0.50 mils (0.013 mm) and 0.75 mils (0.019 mm). Materials from which this microporous membrane can be made include for example, perfluoroalkyloxy (PFA), fluorinated ethylene propylene (FEP), polyolefins, polyamides, cellulotics, polycarbonates, and fluorinated and/or chlorinated polymers, ~~and polysulfones~~. A most preferred material is expanded porous

polytetrafluoroethylene (PTFE) made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566 herein incorporated by reference. This material is commercially available in a variety of forms from W.L. Gore & Associates, Inc., of Elkton, MD, under the trademark GORE-TEX®. The expanded PTFE membrane can be made in a number of ~~thickness~~ thicknesses ranging from 0.00025 inches to 0.125 inches (6 µm to 3 mm) with the preferred thickness for the present invention being at most 1 mil (0.025 mm) and most preferably between 0.50 mils (0.013 mm) and 0.75 mils (0.019 mm). The expanded PTFE membrane can be made with porosities ranging from 20% to 98%, with the preferred porosity for the present invention being 70-95%. Figure 3 shows a photomicrograph of the internal microstructure of expanded PTFE used as the base material.

**REPLACE the paragraph beginning on Page 12, Line 10 with the following:**

The ~~conductivity~~ of the composite membrane was tested to measure the ionic conduction rate in terms of micromhos per minute. This test was performed with two 900 ml. compartments between which the treated membrane was placed. The exposed surface area of membrane was 7.07 sq. in. (45.65 sq. cm). One compartment (the retentate side) was filled with 1 M NaCl solution. The other side (the permeate side) was filled with pure distilled water. Both compartments were stirred continuously and at the same speed with two electric mixers using polypropylene impellers. The ~~conductivity~~ conductance of the permeate side was recorded every 5 minutes for an hour with a hand-held conductivity meter, Omega Model No. PHH80. The total ionic conduction rate was determined by taking the average slope of a graph of ~~conductivity~~ conductance over time.

**REPLACE the paragraph beginning on Page 13, Line 1 with the following:**

Example 1:

A sample of expanded polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566, herein incorporated by reference. The membrane, with a nominal thickness of 0.75 mils (0.02 mm) and a 0.2 micrometer pore size, was mounted on a 6 inch wooden embroidery hoop. A solution was prepared comprising 95% by volume of a perfluorosulfonic ~~acid/tetra-fluoroethylene~~ acid/tetrafluoroethylene copolymer resin (in H<sup>+</sup> form) in a solution of low molecular weight alcohols comprising propanol, butanol, and methanol known as Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% of a nonionic surfactant of octyl phenoxy poly ethoxyethanol known as Triton ~~X-100~~ X-100 commercially available from Rohm & Haas of Philadelphia, PA. This solution was brushed on both sides of the membrane so as to impregnate and substantially occlude the micropore structure. The sample was then dried in the oven at 140<sup>0</sup>C for 30 seconds. The procedure was repeated two more times to fully occlude the micropores. The sample was then soaked in isopropanol for 5 minutes to remove the surfactant. After rinsing with distilled water and allowing to dry at room temperature, a final coat of the Nafion-surfactant solution as described above was applied. The wet membrane was again dried in the oven at 140<sup>0</sup>C for 30 seconds and soaked in isopropanol for 2 minutes. The membrane was finally boiled in distilled water for 10 minutes under atmospheric pressure to swell the treated membrane. Gurley numbers for this material are summarized in Table 3. Ionic conductive rates are summarized in Table 4. The strength modulus may be found in Table 5; percent linear expansion may be found in Table 6; and percent weight change of this sample may be found in Table 7. The swollen membrane was later dried to a dehydrolyzed state in an oven at 140<sup>0</sup>C for 30 seconds. The thickness of the dried composite membrane was measured and found to be approximately the same thickness as the base material.

**REPLACE the paragraph beginning on Page 13, Line 31 through Page 14, Line 12 with the following:**

**Example 2:**

A sample of expanded porous PTFE membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566 having a pore size of 0.2 micrometers and nominal thickness of 0.75 mils (0.02 mm) and a Gurley Densometer air flow of 2-4 seconds was placed on top of a netting of polypropylene obtained from Conwed Plastics Corp. of Minneapolis, MN. The two materials were bonded together on a laminator with 10 psig pressure, a speed of 15 feet per minute and a temperature of 200<sup>0</sup>C. No adhesives were used. The reinforced membrane sample was then placed on a 6 inch wooden embroidery hoop. A solution of 96% by volume of a perfluorosulfonic acid TFE copolymer resin in alcohol Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 4% of the nonionic surfactant Triton X-100 obtained from Rohm & Haas was prepared. This solution was brushed on the membrane side only to substantially occlude the micropores and the sample was dried in an oven at 130<sup>0</sup>C. This procedure was repeated three more times to fully occlude the micropores. The sample was then baked in an oven at 140<sup>0</sup>C for 5 minutes. The sample was soaked in isopropanol for 5 minutes to remove the surfactant. The membrane was then boiled in distilled water for 30 minutes under atmospheric pressure causing the treated membrane to swell. Gurley numbers for this material are summarized in Table 3.

**REPLACE the paragraph beginning on Page 14, Line 18 with the following:**

**Example 3:**

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566, having a thickness of 0.5

mils (0.01 mm) with a pore size of 0.2 micrometer was mounted on a 6 inch wooden embroidery hoop. A solution of 100% Nafion resin solution, perfluorosulfonic acid/TFE copolymer resin in a solvent mixture of propanol, butanol, and methanol known commercially from E.I. DuPont de Nemours, Inc. as Nafion® solution NR-50 (1100 EW) without the addition of any surfactants was brushed onto both sides of the membrane to substantially occlude the micropores. The sample was then placed in an oven at 160°C to dry. This procedure was repeated four more times until the membrane was completely transparent and the micropores were fully occluded. The sample was then boiled in distilled water for 30 minutes at atmospheric pressure causing the membrane to swell. Gurley numbers for this material are summarized in Table 3. The electrical conductivity was measured and summarized in Table 2.

**REPLACE the paragraph beginning on Page 14, Line 35 through Page 15, Line 12 with the following:**

**Example 4:**

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566 having a thickness of 0.5 mils (0.01 mm) and a pore size 0.2 micrometers was mounted on a 6 inch wooden embroidery hoop. A solution of 99% by volume Nafion NR-50 commercially available from E.I. DuPont de Nemours, Inc. and 1% surfactant mixture was prepared. The surfactant mixture consisted of 50% of a nonionic surfactant, Triton X-100 commercially available from Rohm & Haas Corp. and 50% Zonyl FSO commercially available from E.I. DuPont de Nemours, Inc. This solution was brushed on both sides of the membrane and was allowed to dry at room temperature. This procedure was repeated 4 more times until the sample was completely transparent and to fully occlude the micropores. The sample was not treated so as to remove the surfactant. The

composite membrane was boiled in distilled water for 5 minutes causing the membrane to swell.

The Gurley number for this material is summarized in Table 3.

**REPLACE the paragraph beginning on Page 15, Line 14 with the following:**

**Example 5:**

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566, having a thickness of 0.5 mils (0.01 mm) with a pore size of 0.2 micrometer was mounted onto a 6 inch wooden embroidery hoop. A solution of 95% by volume Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% of a nonionic surfactant, Triton X-100 commercially available from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off. The wet membrane was dried in an oven at 140<sup>0</sup>C for 30 seconds. Three additional coats of solution were applied to the membrane in the same manner to fully occlude the micropores. The membrane was then soaked in isopropanol for 2 minutes to remove the surfactant. The membrane was rinsed with distilled water and allowed to dry at room temperature. A final treatment of the Nafion-Triton solution was applied. The wet membrane was dried in the oven at 140<sup>0</sup>C for 30 seconds, then soaked in isopropanol for 2 minutes. Finally, the membrane was boiled in distilled water for 5 minutes. Moisture vapor transmission rates for the treated membrane were measured and are summarized in Table 1. The Gurley number of the treated membrane ~~are~~ is summarized in Table 3.

**REPLACE the paragraph beginning on Page 15, Line 35 through Page 16, Line 14 with the following:**

**Example 6:**



A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~53,593,568~~ 3,953,566, having a nominal thickness of 0.75 mils (0.02 mm) and a pore size of 0.2 micrometers was mounted onto a 6 inch wooden embroidery hoop. The Gurley Densometer air flow on this membrane was 2-4 seconds. A solution of 95% by volume Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% Triton X-100 non-ionic surfactant from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off. The wet membrane was dried in the oven at 140°C for 30 seconds. Three additional coats of solution were applied in the same manner. The membrane was then soaked in isopropanol for 2 minutes. After rinsing with distilled water and allowing to dry at room temperature, a final coat of the Nafion surfactant solution was applied. The wet membrane was dried in the oven at 140°C for 30 seconds, then soaked in isopropanol for 2 minutes. This material was not boiled. No swelling other than the minor swelling during the surfactant removal occurred. The ionic conduction rate for this material is presented in Table 4.

**REPLACE the paragraph beginning on Page 16, Line 16 with the following:**

**Example 7:**

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. ~~3,593,566~~ 3,953,566 having a nominal thickness of 0.75 mils (0.02 mm) and a pore size of 0.2 micrometers was mounted onto a 5 inch plastic embroidery hoop. The Gurley Densometer air flow on this membrane was 2-4 seconds. A solution of 95% by volume Nafion NR-50 (11100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% Triton X-100 non-ionic surfactant from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off.

The wet membrane was dried in the oven at 140<sup>0</sup>C for 30 seconds. Two additional coats of solution were applied in the same manner so as to fully occlude the micropores. The membrane was then soaked in isopropanol for 2 minutes. After rinsing with distilled water and allowing to dry at room temperature, a final coat of the same Nafion NR-50 Triton X-100 solution was applied. The wet membrane was dried in the oven at 140<sup>0</sup>C for 30 seconds and then soaked in isopropanol for 2 minutes to remove the surfactant. The sample was rinsed and dried at room temperature. No boiling occurred.

**REPLACE the paragraph beginning on Page 17, Line 6 with the following:**

Nafion 117, a perfluorosulfonic acid cation exchange membrane, unreinforced film of 1100 equivalent weight commercially available from E.I. DuPont de Nemours Co., Inc., having a quoted nominal thickness of 7 mils (0.18 mm) was obtained. The samples, originally in the hydrated swollen state were measured in the x- and y-directions and weighed. The samples were then dried ~~at room temperature~~ in a convection oven at 140° C for approximately one minute to an unswollen state and then remeasured from which expansion and weight change measurements found in Tables 6 and 7 were calculated. Nafion 115, a perfluorosulfonic acid cation exchange membrane, unreinforced film of 1100 equivalent weight also commercially available from E. I. DuPont de Nemours, Inc., having a nominal thickness of 5 mils (0.1 mm) was obtained. This sample was also obtained commercially in the hydrated swollen state.

**REPLACE the paragraph beginning on Page 17, Line 24 (Table 2) with the following:**

**TABLE 2**

Electrical ~~Conductivity~~ Conductance

Sample ID*	<del>Conductivity</del> <u>Conductance</u> (micromhos)
3	1,277
Nafion 117	1,214

\*Measurements were obtained on samples in their swollen state.